[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE BENZIL REARRANGEMENT. VI

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The rearrangement of benzil to benzilic acid is always accompanied by the formation of more or less benzoic acid. It was shown recently[1] that the proportion of water in the reaction mixture is the chief factor that determines which acid shall predominate. When benzil is dissolved in absolute alcohol, and acted upon by sodium ethoxide, practically no benzilic acid is obtained; the reaction products are benzaldehyde and ethyl benzoate. On the other hand, strong or weak aqueous alkali, or water alone, when heated with benzil yields benzilic acid practically free from benzoic acid.

This difference in behavior was accounted for by the presence or absence of a mobile hydroxyl group in the intermediate addition products which benzil forms with the reagents: with water (*a*) $C_6H_5C(OH)(OH)COC_6H_5$; with sodium hydroxide (*b*) $C_6H_5C(ONa)(OH)COC_6H_5$; and with sodium ethoxide (*c*) $C_6H_5C(ONa)(OC_2H_5)COC_6H_5$. Addition product (*c*) was isolated, and shown to undergo alcoholysis as follows.

$$C_6H_5C(ONa)(OC_2H_5)COC_6H_5 + C_2H_5OH = C_6H_5CHO + C_6H_5COOC_2H_5 + NaOC_2H_5 \quad (1)$$

The groups $-OC_2H_5$ and $-ONa$ are evidently incapable of wandering under the experimental conditions; migration of $-OC_2H_5$ would yield ethyl benzilate, $(C_6H_5)_2C(OH)COOC_2H_5$; shift of $-ONa$ would result in the formation of ethylbenzilic acid, $(C_6H_5)_2C(OC_2H_5)COOH$; but neither substance could be detected.

These experimental findings were confirmed by G. Scheuing[2] during the publication of my paper. Scheuing obtained not only addition product (*c*), but the analogous one with potassium methoxide (*d*), $C_6H_5C(OK)(OCH_3)COC_6H_5$, and also with potassium hydroxide (*e*), $C_6H_5C(OK)(OH)COC_6H_5$.

When (*e*) was heated in benzene suspension to 80°, it was very rapidly, and almost quantitatively, converted into potassium benzilate. On the other hand, (*d*) gave only 6% of benzilate after prolonged heating. Scheuing also looked for methylbenzilic acid, and for methyl benzilate, without success. The formation of benzaldehyde and of methyl benzoate, however, escaped his attention.

The mechanism of the formation of benzoic acid during the benzil rearrangement is clear from the above data. Benzoic acid results from

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[1] Lachman, THIS JOURNAL, 45, 1509 (1923).

[2] Scheuing, *Ber.*, 56B, 253 (1923). This paper was received on October 31, 1922 and published on January 10, 1923. My article was received on January 13, 1923, published in June, 1923. The formation of benzil sodium ethoxide was, however, described by me in a paper received on February 6, 1922, which was refused publication.

the hydrolysis of its ester, which is formed by a rupturing process; and it may also come in part from benzaldehyde. Very recently, however, an article by Schönberg and Keller[3] has appeared, which ascribes the formation of benzoic acid to oxidation by atmospheric oxygen.

$$C_6H_5COCOC_6H_5 + O + H_2O = 2C_6H_5COOH \qquad (2)$$

The authors give elaborate directions to exclude air during the preparation of benzilic acid, but offer no evidence of this oxidation mechanism. It is easy to show that air plays no part in the production of benzoic acid from benzil.

A solution of 3 g. of benzil in 35 cc. of ether was added to a solution of 1.7 g. of sodium hydroxide in 15 cc. of 97% alcohol; and according to the instructions of Schönberg and Keller, the mixture was placed in a 50cc. flask, and sufficient ether added to fill it completely to the stopper. A duplicate lot was placed in a liter flask, which contained more than sufficient air to oxidize completely 3 g. of benzil according to Equation 2. After standing overnight at room temperature, the material in the 50cc. flask gave 3.0 g. of acids, that in the liter flask 3.1 g. By indirect analysis[4] they were found to vary but slightly in their percentages of benzoic acid (10% and 11%, respectively).

Under the conditions chosen by Schönberg and Keller for the benzil rearrangement, a benzilic acid of fairly high purity is rapidly formed in the cold. There is an apparent discrepancy between their results and those previously reported by me with respect to the percentage of water necessary to effect metakliny. The investigation of this discrepancy has led to interesting results. When the amount of water present is small, a change of solvent from ether to alcohol is paralleled by replacement of benzilic acid by benzoic acid. The following table is instructive.

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[3] Schönberg and Keller, *Ber.*, **56B**, 1638 (1923). This paper was received on April 27, 1923, and published on July 4, 1923. The authors were acquainted with Scheuing's work, but could not have known of mine.

[4] Schönberg and Keller ascertained the purity of their acid products by titration, on the assumption that only benzilic and benzoic acids are present. This assumption is incorrect; the precipitated acids always contain ethyldibenzil [compare Lachman, THIS JOURNAL, **46**, 708 (1924)]. Ethyldibenzil probably has a molecular weight of 494; it is, however, a very weak acid, and by titration gives an apparent molecular weight of 355, which almost exactly compensates an equal weight of benzoic acid (mol. wt., 122). Such a mixture would show an apparent molecular weight of 238; that of benzilic acid is 228. The following analytical data were obtained with the two samples mentioned above.

	Wt.	Ethyldibenzil	Corr. wt.	Cc. of 0.1 *N* alkali	Apparent mol. wt.	Benzoic acid, %
50 cc........	**0.5042**	0.0431	0.4611	21.2	217	10
Liter........	**.3515**	.0278	.3237	15.0	216	11

To separate from ethyldibenzil, the crude acid sample is extracted with hot water; ethyldibenzil is collected on a tared filter; the acids are then titrated in the filtrate.

In each case, 2.1 g. of benzil (0.01 molecular equivalent) was taken. The solvents were carefully dried, and redistilled with precautions against atmospheric moisture, and were measured under similar protection. Although the presence or absence of air had been found to be unimportant, the flasks in this series were filled to the stopper. The mixtures stood for four days at room temperature. They were then diluted with sodium bicarbonate solution, to keep down the hydroxyl-ion concentration, and extracted twice with ether; and the combined ether extracts were washed once with water, which was added to the carbonate solution. The latter was concentrated to about 50 cc., and precipitated by addition of a slight excess of hydrochloric acid. The acids were weighed, and analyzed as described above. All of the ether extracts contained benzaldehyde, ethyl benzoate and benzil, which were not separately estimated.

Table I

Effect of Ether on the Benzil Rearrangement

Alcohol Cc.	Ether Cc.	Water Cc.	NaOEt Mol. eq.	Acids G.	Insol. G.	Mol. wt. of soluble acid	Benzoic acid %
100	..	.	0.01	0.005	...	...	..
98	..	2	.01	.35	0.01	131	91
100	..	.	.03	.20	.01	134	88
98	..	2	.03	1.05	.02	133	89
50	50	.	.01	0.005	...	...	..
48	50	2	.01	.27	.04	224	4
50	50	.	.03	.48	.07	222	6
48	50	2	.03	1.70	.22	223	5

Brief mention may also be made of a further factor in the benzil rearrangement; potassium hydroxide acts very much faster than does sodium hydroxide. Using 1 molecular equivalent of potassium (in 97% alcohol), Schönberg and Keller found about 80% conversion into benzilic acid in two hours; on repeating as nearly as possible their conditions, with replacement of potassium by sodium, I obtained only 55% in 24 hours.

A similar marked difference was noted in acting upon 5 g. of benzil, dissolved in 90 cc. of ether, with 1 equivalent of the two metals dissolved in 10 cc. of commercial absolute alcohol (about 99%). After three hours at room temperature, the mixture containing potassium gave 0.9 g. of benzilic acid; the lot with sodium gave no measurable amount of acid, and 4.9 g. of benzil was recovered.

Conclusion

In the benzil rearrangement we are dealing with two competing reactions: metakliny,[5] giving benzilic acid; and rupture, which produces benzaldehyde and benzoic ester, both of which may subsequently appear as benzoic acid. Metakliny will not occur in the absence of water; but a much

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[5] Lachman, This Journal, **44**, 338 (1922).

smaller amount of water will suffice, if ether is used as a part of the solvent, and if potassium hydroxide is employed in place of sodium hydroxide.

The difference in reactivity between potassium and sodium is not unusual, although it is more marked in this instance than is generally observed. The effect of ether is more difficult to account for. The most plausible explanation would seem to be the increased fugacity of water in ether solution. The tendency of reaction rates to vary with change of solvent has been carefully studied by Bugarszky,[6] but no general conclusions seem to have been reached as yet.

The present instance is an unusually striking illustration of the solvent effect, resulting as it does in a nearly complete change of the reaction product.[7]

Summary

1. A recent publication ascribes the formation of benzoic acid during the benzil rearrangement, to oxidation by atmospheric oxygen. It is shown that such an action does not occur.
2. The production of benzoic acid varies inversely with the amount of water present in the reacting mixture; as the proportion of water increases, less benzoic, but more benzilic, acid results.
3. Less water is required for the same effect when potassium hydroxide is used in place of sodium hydroxide.
4. Substitution of ether for alcohol as a solvent enormously enhances the reactivity of water in the benzil rearrangement.

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[6] Bugarszky, *Z. physik. Chem.*, 71, 705 (1910).

[7] Students frequently have difficulty in visualizing how the acceleration of one of two competing reactions should act to suppress the other. We may liken this to a bucket containing a fixed amount of water, with two small holes draining into separate pails. Each pail will get its share of the water, depending on the size of the holes; but if one hole is greatly enlarged, much less water will flow into the pail fed by the other.